Class---B.Sc. Part III

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Paper---VI

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COMPERATIVE CHEMISTRY OF CHROMIUM, MOLYBDENUM AND TUNGSTEN:

OXIDATION STATES:

The ground state of Chromium and Molybdenum are d^5s^1, with stable half- filled configuration, whilst Tungsten has a d^4s^2 arrangement. From the electronic structure Cr and Mo have (+I) to (+VI) whereas W have (+II) to (+VI) oxidation states. Cr. (+II) is reducing, Cr((+III) is the most stable and important and Cr(+IV) is strongly oxidising. The stable states for Mo and W are (+VI) though Mo (+V) and W(+V) are stable in water. Cr(+VI) is strongly oxidising whereas Mo(+VI) and W (+VI) are stable. SimilarlyCr(+III) are very stable but Mo(+III) and W(+III) are strongly reducing. This property is usual as we go down a group, the higher oxidation state become more stable and the lower oxidation states become less stable. The Compounds of all the three metals are given below:

(+II)	(+III)	(+IV)	(+V)	(+VI)
	Cr_2O_3	CrO_2		CrO_3
		MoO_2	Mo_2O_5	MoO_3
		WO_2		WO_3
CrF_2	CrF_3	CrF_4	CrF_5	
$CrCl_2$	$CrCl_3$	$CrCl_4$		
$CrBr_2$	$CrBr_3$	$CrBr_4$		
CrI_2	CrI_3	CrI_4		
	MoF_3	MoF_4	MoF_5	MoF_6

$MoCl_2$	$MoCl_3$	$MoCl_4$	$MoCl_5$	
MoI_2	MoI_3			
		WF_4	WF_5	WF_6
WCl_2	WCl_3	WCl_4	WCl_5	WCl_6
WBr_2	WBr_3	WBr_4	WBr_5	WBr_6
WI_2	WI_3			

(+IV) State:

A limited number of Cr(+IV) compounds are known. These are very strong oxidising agents, they are $(CrO_4)^{-2}$, dichromate (Cr_2O_7), chromium trioxide (CrO_3), oxohalidesCrO_3X^-, CrO_2X_2, (X= F, Cl, Br or I) $CrOX_4$ (X = F or Cl) and CrF_6 .

MoO_3 and WO_3 are formed. They are acidic and not attacked by acid except HF, but they are dissolved in NaOH forming MoO_4^{2-}, and WO_4^{2-} ions. The oxides of Mo and W differ with of chromium in several ways:

i)They have almost no oxidising properties.

ii)They are insoluble in water.

iii)Their melting point is much higher Cro_3 = 197°C, MoO_3 =795°C and WO_3 = 1473°C.

iv) Their colour and structure are different.

(+V) State:

There are few Cr(+V) compounds are known, they are unstable and decompose to Cr(+III) and Cr(+VI) compounds. Examples are CrF_5, K_3CrO_8

MoF_5 has a tetrameric structure of four octahedra joined into a ring .MO_2Cl_{10} is also known compound. Tungsten have WX_5 (X= F, Cl, Br) compounds.

(+IV) State:

Chromium (+IV) compounds are very rare .CrF_4 , CrO_2 , $CrOF_2$ is known compound . CrO_2 is black in colour and has some metallic conductivity. It is also ferromagnetic and is widely used to mack high quality magnetic recording tapes.

MoO_2 and WO_2 are well known compounds.

(+III) State:

(+III) Oxidation state of chromium is the most important and most stable compound of chromium. These compounds are very stable in an acidic solution but it is easily oxidised to (+VI) state in alkaline solution. Cr_2O_3 is a green solid which is used as a pigment. All the anhydrous CrX_3 halides are known. Cr^{3+} ions form an enormous number and variety of complexes.

Mo^{3+} andW^{3+} do not exist as oxides, but all halides i. e MoX_3 (X= F, Cl, Br or I) are known except WF_3. These compounds do not contain simple ions. Mo(+III) are fairly stable, but slowly oxidised in air and hydrolysed in water. They form octahedral complexes with halide ion in solution.

(+II) State:

Cr(+II) compounds are well known $[Cr(H_2O)_6]^{2+}$ ion is sky blue coloured and one of the strongest reducing agents known in aqueous solution. Cr(+II) ion may stabilize by forming complex compounds.

CrX_2 (X = F, Cl, Br or I) are well known compounds. Mo and W do not form difluorides but MX_2 (Cl, Br and I) are known. They are usually made by reduction or thermal decomposition) of higher halides. They do not exist in simple ion but form cluster compounds.

(+I) States:

The oxidation state (+I) expected for the atoms with a d^5s^1 configuration is very uncommon. Trisdipyridyl Chromium (I) perchlorate $[Cr(dipyridyl)_3]^+Clo^-$ is known Mo and W form sandwich type structures.

Zero State, (-I) and(-II) state

The zero oxidation arises in metal carbonyl such as $M(CO)_6$, where the б – bonding electrons are donated by the CO group to the meta and strong d_π-p_π back bonding occurs from the filled metal orbitals.